THE LIME INDUSTRY

BY OLIVER BOWLES

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Oliver Bowles[1/]

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PREFACE

The major part of this circular is adapted with modifications from a Bureau of Mines information circular prepared in 1936 and revised in 1941.2/ Much of the information is fundamental, and there was little change in those years. The statistical sections of the previous report have been largely omitted because, first, statistics rapidly become obsolete, and, second, they are available each year in the Lime chapters in the Bureau of Mines Minerals Yearbook. Trends in production, distribution, and use may be followed by consulting those chapters in conjunction with the data on trends in this report.

INTRODUCTION

Manufacture of lime is one of the oldest industries. Plants are distributed widely and furnish an essential raw material for numerous commodities. Use of lime in hundreds of manufacturing and chemical processes, by the building trades, and in agriculture has created a demand for large production and has necessitated exhaustive research on methods of manufacture and uses. The bibliography of publications on lime is extensive; but, for the most part, each publication has dealt with individual operations.

The purpose of this paper is to present a general picture of the industry as a whole. The abundant literature has been abstracted and quoted freely, and the National Lime Association has furnished valuable data for certain sections. Publications containing more-detailed information on the various branches of the industry are referred to in the footnotes and bibliography.

DEFINITION

Lime may be defined as calcium oxide resulting from heating calcium carbonate to a temperature at which the carbon dioxide is removed. A hundred pounds of pure calcium carbonate ($CaCO_3$) will yield 56 pounds of lime (CaO). The most common form of calcium carbonate in nature is limestone; therefore limestone is the chief raw material used to manufacture lime. In many places limestone is associated with varying quantities of calcium-magnesium carbonate (the mineral dolomite), or a deposit may consist of virtually pure dolomite. Calcination of such rocks produces mixed oxides of calcium and magnesium, which also are regarded as lime. Limestone almost always contains impurities, such as silica and oxides of iron and aluminum. Commercial limes usually contain not more than 5 percent total impurities; except in certain exacting chemical or industrial processes, magnesia is not considered an impurity.

2/ Bowles, Oliver, and Banks, D. M., Lime: Bureau of Mines Inf. Circ. 6884R, 1936 (revised 1941 by Duncan McConnell), 48 pp.

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Slaked or hydrated lime is calcium hydroxide ($Ca(OH)_2$) formed by reaction between quicklime and water. The term "lime" more properly refers to quicklime (CaO or mixtures of CaO and MgO), but it is sometimes used in a more general sense to include slaked or hydrated lime also. The term "lime" should not be applied to limestone or calcium carbonate. Because of their tendency to combine with other substances, neither quicklime nor hydrated lime occurs in nature.

Air-slaked lime results when either quicklime or hydrated lime is allowed to remain in contact with air for a considerable time. Both moisture and carbon dioxide are absorbed during air-slaking, and a product that will not "set" may result.

Varieties

Limes are classified according to their composition as follows:

High-calcium lime, containing not less than 90 percent calcium oxide and 0 to 5 percent magnesia.

Low-magnesium lime, containing 5 to 25 percent magnesia.

Dolomitic or high-magnesium lime, containing 25 to 45 percent magnesia.

A magnesia content of 45 percent is the maximum that can be obtained by calcining a pure dolomite. To obtain more than that amount from carbonate rocks, a magnesite ($MgCO_3$) or a mixture of dolomite and magnesite must be calcined; and, except in California, Washington, and Nevada, such materials are uncommon in the United States.

Hydraulic lime results from calcination of limestone containing enough argillaceous matter to form a substance that will set under water. Its action is similar to that of natural cement, but it contains more calcium and less aluminum.

Chemical and Physical Properties

Commercial limes are composed of calcium oxide, anywhere from 0 to 45 percent magnesium oxide, and generally less than 5 percent impurities, such as silica and oxides of iron and aluminum. When properly burned and fresh from the kiln, lime should contain virtually no water and less than 0.5 percent carbon dioxide. If the impurities formed by the contact of lime with the lining of a kiln and materials introduced by the ash content of fuel (in rotary and shaft kilns) are disregarded, the chemical composition of any lime will be the same as that of the stone from which it was burned, minus the carbon dioxide; but the proportion of impurities in the stone will be nearly doubled in the lime because of the loss of about half the weight of the stone as carbon dioxide during burning. Therefore, a chemical analysis of a limestone is a very good criterion of the grade and commercial utility of the lime it will produce. Commercial limes in the United States are chiefly the high-calcium and dolomitic types, with analyses ranging from 0.5

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to 2.5 percent magnesium oxide for the high-calcium types to 35 to 40 percent magnesium oxide for the dolomitic varieties. Total impurities generally are under 5 percent.

Lump lime retains the same form as the stone after calcination, but the porosity is increased greatly. When water is added to lime, a chemical reaction takes place, forming calcium hydroxide ($Ca(OH)_2$), also known as hydrated lime. This process is known as slaking or hydrating and generates considerable heat during the reaction. The reactions of dolomitic lime and high-calcium lime differ somewhat in the slaking process. A high-calcium quicklime expands greatly when water is added. Dolomitic lime slakes much more slowly, generates less heat, and expands less, which results in a correspondingly smaller volume yield. Other things being equal, the less magnesium oxide in a lime, the more quickly will it slake and the greater will be the amount of heat generated.

The rate of hydration depends also on the porosity of the lime. Water penetrates the more porous limes rapidly, and chemical reaction takes place quickly. In some cases the porosity of a lime seems to be a greater factor than the chemical composition; for instance, a very porous dolomitic lime may slake more quickly than a dense lime with a much higher content of calcium oxide.

When quicklime is underburned the calcium carbonate left acts as inert matter for most uses. Overburned lime also contains relatively inactive matter, consisting of a combination of lime with the impurities, forming a semivitrified mass. When overburned, lime is inclined to slake slowly because of the diminution of pore space. The appearance of underburned lime varies with that of the stone used and can be distinguished only by one who has had experience in burning the particular kind of stone. Overburned quicklime generally is yellow or black and can be separated readily from good lime.

When quicklime is exposed to air, it absorbs carbon dioxide and water and air-slakes. This reaction takes place in two more or less distinct stages - first, absorption of water and second, displacement of the water by carbon dioxide. As these reactions are slow, lime may air-slake to almost any degree, and this has led to great confusion in the literature regarding the properties of air-slaked lime. For instance, at one stage of the process, when the water has been absorbed and has not been displaced to any extent, the product is similar in composition to water-slaked or hydrated lime. At the other extreme, recarbonation may be so nearly complete that the lime virtually has reverted to limestone. Absorption of water during air-slaking involves a large increase in volume, and the lumps of lime therefore fall to pieces.

Limestone may fall to pieces in the kiln under several circumstances: The stone may be so soft that it is broken by abrasion; its pores may be filled with water at the time of burning, which shatters the stone when heated; or its component crystals may be bound together by organic matter that is consumed in the kiln. Sometimes over 50 percent of the output of

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a kiln is finely divided lime, which is as good for most purposes as lump lime and is easier to handle.

The chemical and physical properties of a lime, which determine its adaptability for various processes and products, have been the subject of much scientific study. It has been found that properties may be adjusted to some extent during quarrying and manufacture. The limiting ratio of calcium to magnesium depends largely on the market in the particular locality. When the lime is sold for chemical purposes, this ratio generally will be specified. Specifications for the various uses are discussed under Uses and Tests and Standards.

HISTORY OF THE INDUSTRY

Lime has been made and used since ancient times, and evidence of its use can be traced back through the Roman, Greek, and Egyptian civilizations. Use of kilns for burning was mentioned by Cato in 184 B. C. Lime mortar was used in the pyramids of Cheops and older monuments, and references have been found indicating that lime was used at this early time in the chemical as well as the building industries. Recent investigations of a Roman water conduit, A. D. 70-100, running from Eifel to Cologne showed that the concrete was made with hydraulic lime, Rhine sand, and crushed, high-calcium limestone.3/ Something of the manufacture and use of lime may be traced from passages in the Old Testament, from the writings of Dioscoridos and Pliny (circa A. D. 75) and of Vitruvius (circa 50 B. C.), and from references in literature to its use in war and by alchemists during the Middle Ages. Joseph Black and Lavoisier (circa 1777) dispelled the old theory that calcination was attributable to the introduction of phlogiston. The first measurements of the dissociation pressure of calcium carbonate were made in the latter part of the nineteenth century by Debray and Le Chatelier.

Although machinery and methods of preparing limestone for burning were developed to pace the growth of an industry that has reached large proportions, comparatively little improvement was made in the process of burning lime or in the type of kiln used until recent years. Within the past 60 years, experiments in the laboratory and field have resulted in the adoption of certain improvements. The outstanding feature in the development of the industry was the manufacture of hydrated lime, which began about 1900, and the rapid growth of its use. One of the more recent advances in lime manufacture was introduction of pulverized quicklime. This product has been received favorably and is used widely. New types of kilns and hydrators have been evolved, and pressure hydration of dolomitic lime is an important development. The rotary kiln, well-known in the cement industry, has been adopted extensively for burning lime and produces what is commonly called pebble lime.

A valuable contribution to the lime industry was a study by the National Bureau of Standards, beginning in 1912. In cooperation with the lime-consuming industries, it conducted extensive research to determine what kinds

3/ Quarry Manager's Journal, Ancient Lime Mortar Concrete: Vol. 18, No. 3, June 1935, p. 81

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of lime are most efficient and economical for each product or process of manufacture. The result of this work was the promulgation of many specifications. The Bureau of Standards also made detailed studies of typical lime plants and in 1913 published a paper on the manufacture of lime,4/ which was revised in 1927.5/ Much progress has been made during subsequent years on equipment and methods used in mining the stone and calcining it into lime. Some of the improvements are covered in following sections of this report, and for more detailed information the reader is referred to articles recorded in the bibliography.

Statistical records of the lime industry since 1894 are available in annual reports published, first, by the Federal Geological Survey and later, by the Federal Bureau of Mines. A promotional and research organization for the lime industry has existed since 1902, and its activities have had an important influence on the development of the industry. Before 1918 this work was carried on by the National Lime Manufacturers' Association and the Hydrated Lime Bureau. In 1918 the National Lime Association was organized and it was incorporated in 1922.

RAW MATERIALS

The natural calcium and magnesium carbonates - limestone, marble, dolomite, and shell deposits - are the principal sources of commercial lime. Small quantities are made from similar carbonates produced as byproducts of chemical industries. Of these materials, limestone is the most abundant and is used most extensively for lime manufacture.

Limestone

Origin

Limestone is formed in beds by chemical or biochemical precipitation of calcium carbonate or by the accumulation of calcareous shells. Varying quantities of other substances, such as magnesium carbonate, silica, clayey material, salts of iron, and organic matter, may be present as impurities. Calcareous materials are consolidated gradually into rock by compaction, dehydration, and crystallization, and, through long geologic ages of surface adjustment, they occupy land areas and become available for commercial use.

Composition and Varieties

The chemical composition of limestone for making lime is important, as lime is used in many products and processes in which the chemical requirements are exacting. Physical properties have some influence on methods of manufacture and on costs. For instance, a friable stone is unsuitable for shaft kilns because it crumbles, retards the draft, and furnishes a small proportion of lump lime. High porosity may retard the rate of heat conductivity and thus lower fuel ratios.

4/ Emley, W. E., Manufacture of Lime: Nat. Bureau of Standards Technol. Paper 16, 1916, 130 pp.

5/ National Bureau of Standards, Manufacture of Lime: Circ. 337, 1927, 104 pp.

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The essential chemical constituent of limestone is calcium carbonate ($CaCO_3$), the mineral calcite. Many commercial occurrences designated high-calcium limestone carry 93 to 99 percent calcium carbonate. When other substances occur in the stone, it is classed according to the nature of the impurities. If 10 percent magnesium carbonate is present it is called magnesian or dolomitic limestone. Magnesian limestones may embrace several varieties texturally and if physically suitable may be burned to lime, which will be a mixture of calcium oxide (CaO) and magnesium oxide (MgO). When the amount of magnesium carbonate present approaches 45 percent, the rock is known as dolomite, which is the double carbonate of calcium and magnesium, expressed by the formula $CaCO_3.MgCO_3$.

Argillaceous limestone contains a considerable proportion of clay, consisting mainly of aluminum silicate. If clay is present in certain proportions, mortar made with the lime burned from the stone has the property of setting under water, and the lime is said to be hydraulic. Siliceous or cherty varieties contain considerable silica; if the limestone contains 2 percent or more, it rarely is suitable for making lime. Ferruginous limestone has considerable iron content. Carbonaceous or bituminous limestone contains carbonaceous matter, such as peat or other organic materials, which color the rock a dark gray or black. Moderate amounts of carbonaceous matter are not retained in the lime, as they are consumed during calcination.

Other varieties of limestone are based on texture or physical character. Common compact limestone is a fine-grained, dense, homogeneous, light-gray to almost black aggregate. This variety, when of suitable chemical composition, is burned into lime in many places. Oolitic limestone is composed of small, rounded grains of lime carbonate with a concentrically laminated structure. Some limestone beds have been formed under conditions that have left many shells almost intact or, at least, in fragments well enough preserved to indicate their origin and character. These are known as fossiliferous limestones. Some of them are made up almost entirely of shells of one kind and are named accordingly. Coral, crinoid, and coquina are common types. Unconsolidated oystershell beds are related closely to fossiliferous limestone and are quite extensive. When pure enough, fossiliferous limestone generally is suitable for making lime. Cherty limestone contains nodules and bands of chert or flint and is unsuitable for lime manufacture unless the chert can be separated and removed at very little expense.

Impurities

The common impurities in limestone are clay, which contains silica and alumina; sand or other forms of free silica; iron oxide; iron carbonate; pyrite or marcasite (sulfides of iron); gypsum; alkali salts; and carbonaceous material.

Clay is found most often along the bedding planes, but it also is disseminated through the rock. Silica occurs in hard limestone as nodules or masses of chert (flint) or combined with alumina as clay matter. In soft limestone, such as marl and chalk, silica usually occurs as grains of sand, but certain beds of Cretaceous chalk, notable the deposits along the English

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channel and to a smaller extent in Texas, carry an abundance of chert nodules. Iron compounds are disseminated with the original sediments, but they were brought in by percolating waters and resulted from chemical action with other minerals. Sulfur is present in combination with iron as pyrite or marcasite and in gypsum ($CaSO_4.2H_2O$), so that under ordinary conditions it is not free. However, these sulfides are easily oxidized. Some limestone contains small quantities of the alkalies, soda and potash, probably in the form of carbonates or in the clay impurities as silicates. Impurities are noted in greater proportions in weathered than in unweathered rock because they are less soluble than the limestone.

Impurities in the stone have various effects on the properties of lime. Small amounts of silica tend to decrease the plasticity, sand-carrying capacity, and yield of a lime but have no apparent effect on its hardness or strength. The same may be said of iron, except that lime containing large amounts is much stronger and harder. Kaolin seems to act in a manner similar to silica and iron. Gypsum is detrimental, even when only 1 percent is present.

Dolomite

Dolomite is next in importance to limestone as raw material for lime. Magnesium limestone containing 20 percent or more magnesium carbonate is designated dolomitic or high-magnesium limestone. When the quantity of magnesium carbonate approaches 45 percent, the rock is virtually a pure dolomite and is regarded as a distinct mineral composed of calcium and magnesium carbonates combined in proportions expressed by the formula $CaCO_3.MgCO_3$. Dolomite looks like high-calcium limestone but does not liberate carbon dioxide as readily when tested with acid. There is reason to believe that fossiliferous dolomites were originally limestone that was changed to dolomite by magnesium-bearing solutions. These dolomitic limestones are likely to show variations in chemical composition from place to place.

Other Raw Materials

The crystalline or metamorphosed form of limestone known as marble is a common source of lime. As shown later in more detail, marble is or has been used to manufacture lime in New England, Maryland, Tennessee, Washington, and several other States. Waste from many quarries producing building and monumental marble is utilized in this way. Vein deposits of calcite also are used to a limited extent for lime. Marble like limestone may be dolomitic.

Oystershells are one of the purest forms of calcium carbonate that occur in commercial quantities. Therefore, they are well-suited for making chemical lime, for which purity and uniformity of composition are necessary. Easily accessible shell reefs large enough and of a character to warrant their use for lime are few, but their utilization for this purpose has increased in recent years, particularly in the Texas and Louisiana Gulf Coast areas.

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Travertine or calc sinter, a massive, porous to compact limestone, is formed as deposits from solution at calcareous springs. It does not occur extensively in the United States.

Marl, a fine-grained, loose, earthy material consisting essentially of calcium carbonate, occurs commonly; but, because of its high water content and the difficulty in burning, it is not used for making lime. However, it is applied directly to the soil.

Distribution of Limestone in the United States

Deposits of limestone occur in every State and in 1950 were utilized in every State except Delaware, New Hampshire, and North Dakota. In some States the deposits are very extensive and are quarried in hundreds of places for various uses. Distribution of limestone, by States, has been described in some detail by Bowles.6/ Distribution of raw materials suitable for lime manufacture, with chief emphasis on deposits now or recently used, is covered briefly in the following paragraphs.

New England States

Most of the limestone in the New England States is so highly crystalline as to be classed as marble. In Maine the lime industry is centered at Rockland, where vertical or steeply dipping beds of crystalline limestone are utilized extensively. An occurrence of noncrystalline limestone in Aroostook County also has been utilized. In Vermont noncrystalline limestone is found principally in the northwestern counties, where moderate-size lime plants are operated. Waste marble from quarries in Rutland County has been used as raw material. Limestone in the northern part of Rhode Island near Lime Rock has been used to manufacture low-magnesium lime. Large lime plants in western Connecticut and Massachusetts process crystalline limestones and dolomites. Small outcrops of limestone in New Hampshire have no commercial importance at present.

New York, New Jersey, and Pennsylvania

New York and Pennsylvania are especially rich in limestones. In New York they occur extensively in the counties between the Adirondacks and Lake Ontario, and highly pure dolomitic marbles occur in St. Lawrence County. Limestones also outcrop to the south in Herkimer, Saratoga, Washington, and Warren Counties and in a small area in the Champlain Valley. Another formation, containing stone of 95 percent or more calcium carbonate, outcrops at various points in the eastern Adirondacks from Saratoga County northward to the Canadian boundary. Along the lower Hudson a formation outcrops near Poughkeepsie. Limestone beds extend from Otsego County northwestward to Oneida Lake and westward to the Niagara district. Another belt extends from Buffalo in Erie County east to Oneida County and southeast to Albany County, where it curves south toward the Delaware River, and stone suitable for lime

6/ Bowles, Oliver, The Stone Industries: McGraw-Hill Book Co., 2d ed., 1939, pp. 396-452.

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manufacture is found in the Finger Lakes district. Many of the limestones in New York, especially in the western half of the State, are high in calcium carbonate. Although limestones suitable for lime manufacture are abundant in New York, there are few active lime plants in the State.

Commercial high-calcium and magnesium limestones are found in the northwestern border counties of New Jersey, and dolomitic limestone occurs in Somerset County.

In Pennsylvania the high-grade limestones of greatest commercial importance are confined to the central and southeastern counties and to an area north of Pittsburgh near the western border. Extensive deposits of both high-calcium and dolomitic rock occur, the magnesium rock being especially abundant in the valleys of the southeastern section and the high-calcium variety in the central part. Pennsylvania has more lime plants than any other State, but lime is manufactured most extensively in the central and southeastern sections.

Maryland, Delaware, Virginia, West Virginia, North Carolina, and South Carolina

The limestones of this area fall physically into three groups: (1) Hard, nonmetamorphosed limestones of the Appalachian valleys; (2) hard, metamorphosed or crystalline limestones of the Piedmont region; and (3) soft limestones of the Coastal Plain.

The great limestone deposits of the Shenandoah Valley of Virginia and similar valleys lying northwest of the Blue Ridge Mountains are the most noteworthy in this area. The stone of the two western tiers of counties throughout the entire length of Virginia has great commercial value. It is easily accessible and is used extensively for lime. Valuable information on the limestones of the valley of Virginia, West Virginia, and Maryland, as well as those in certain sections of Pennyslvania, Ohio, Illinois, Indiana, and New York, has been published.7/ Limestones of variable composition occur also in the Alleghany Mountains of Virginia. Occurrences in the Piedmont district of the State, especially in Loudoun County, have been utilized for lime. The soft limestones of the Coastal Plain of Virginia consist largely of shell marl. One lime plant in the Norfolk area uses oystershells.

Deposits of hard limestone are found west of the Alleghanies in eastern West Virginia, but few approach in purity those of the northeastern Panhandle.

Tennessee, Mississippi, Alabama, Georgia, and Florida

Limestone deposits are extensive in Tennessee, particularly in the eastern and central parts. The Holston marble of Knox County is the principal source of lime. The limestone of middle Tennessee, which is pure to

7/ Baltimore & Ohio Railroad, High-Calcium Limestones in the Area Served by the Baltimore & Ohio Railroad: Baltimore Md., 1951.

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argillaceous and low in magnesia, is used for lime manufacture in the counties of the central basin. The most prominent formation in the northern and western counties of middle Tennessee contains high-grade limestone in places, which is utilized for lime also. Small beds of limestone and larger deposits of chalk occur in Mississippi, but they are not used to produce lime.

Limestone pure enough for lime production occurs in the river valleys of northern and central Alabama, and highly pure stone outcrops along the sides and bases of plateaus in the same general region. An unusually pure, high-calcium marble occurs in Talladega County. Formations suitable for lime production also occur in the north-central counties of the State. The Selma chalk deposits extending across central Alabama and the Vicksburg limestone farther south are not used for lime. Lime is produced principally in Blount, Shelby, and other counties of the Birmingham area and in the northwest.

In Georgia sources of raw material for lime are confined to the marble belt of Pickens and adjacent counties and the abundant limestones of the Appalachian Valley district to the west. Recent production has been confined to Bartow County.

Limestone is distributed widely in Florida. High-calcium stone, some of which is soft and chalklike, occurs in Jackson County and over a wide area of central Florida, and a compact, white rock, quite hard in places, is found in northwestern Florida. Tampa limestone, a fairly hard, compact, light-gray to yellow rock, occurs in parts of the west-central counties. Coral and oölitic limestones form the foundation of the Keys from Miami to Key West and border the east side of the Everglades. Coquina and related shell varieties are spread over a large part of southern Florida, as well as sections of several northern counties, particularly along the coast. Most Florida limestones are too soft for lime manufacture by ordinary methods; and, at present, the industry is confined to Marion County and to reuse of lime carbonate sludge at the Miami water-supply station.

Wisconsin and Michigan

Limestone deposits are extensive in the north-central and northern sections of Wisconsin, appear in a broad belt along the eastern border of the State, extending across the southern part, and are available in certain areas along the western side. Nearly all of them are dolomites well-adapted for making high-magnesium and special limes. The lime industry, however, is confined chiefly to the east-central counties.

In Michigan limestones border the northern part of the Southern Peninsula along Lakes Michigan and Huron and cross the southeastern part. The largest area is near Rogers City, Presque Isle County. Another important formation outcrops on the east side of Saginaw Bay, on Charity Island in Saginaw Bay, and in Arenac, Eaton, and Jackson Counties. Limestone also occurs along the southern border of the Northern Peninsula. Lime is manufactured at Ludington and Menominee. Rock is shipped to Menominee from Rogers City, and large quantities of Michigan limestone are shipped to lime-manufacturing plants in other States.

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Illinois, Indiana, Ohio, and Kentucky

Commercial limestones of both the high-calcium and dolomitic varieties occur in about a third of the area of Illinois, including the northern end and a belt along the western and southern borders. Scattered deposits of minor economic importance are found in the remaining two-thirds of the State. Lime production is centered chiefly near Quincy, Chicago, and St. Louis.

Limestones occur widely in Indiana, the most important beds forming a belt about 20 miles wide extending northwestward through the central part of the State, including the famous oölitic building limestone quarried in Lawrence and Monroe Counties. Waste from the quarries has been used for lime. Owen, Crawford, Harrison, and Washington Counties also have deposits of high-calcium oölitic limestone, which is burned into lime in Crawford County. Farther north, magnesium limestone occurs in several counties.

Limestone underlies a large part of Ohio and is used extensively for lime manufacture. Exceptionally pure dolomite is found in the Toledo district, including Wood, Sandusky, Ottawa, and several other counties, and most of the lime plants are in this area. A second area farther south, extending as far as Columbus, has extensive deposits of high-calcium and low-magnesium limestones, which are used for lime in many places. High-calcium limestone in eastern Ohio and dolomite in Adams County, southern Ohio, also are used for lime.

Kentucky is underlain with the same limestone formations that occur in Illinois, Indiana, and Ohio, and they appear in many eastern, southeastern, central, north-central, and western counties. Warren County has a notable outcrop of a high-calcium oölitic variety, and lime has been manufactured in Rockcastle and Franklin Counties.

States West of the Mississippi River

In Minnesota commercial limestone occurs only in the southeastern part. The beds generally are highly magnesian, and many are nearly pure dolomites. The only lime made in the State is from stone shipped from Michigan and calcined at Duluth.

The only limestone formations in North Dakota are soft, argillaceous, chalklike beds in the far north, and thin, more or less cherty beds, which occur as the upper strata on buttes in the western area. They are unsuitable for lime manufacture.

Hard limestones occur in the Black Hills district of South Dakota, and production of lime in the State has been confined to this district. The chalky limestone in the eastern part of the State has no commercial use at present.

Limestone is plentiful in Iowa. Formations in the eastern counties are generally high in magnesium; those in the east-central area are magnesian in the north and high-calcium in the south; and those of the central and

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southern parts have some fairly high calcium stone. Chalk beds occur in the western part of the State. Lime has been produced in Jackson and Marion Counties.

The limestones of greatest economic value in Nebraska outcrop chiefly in the southeastern counties, where lime has been produced. Another formation is exposed along the Missouri River in northeastern Nebraska and in the Republican Valley in the southern part.

Dolomite limestone is found in southeastern Missouri, except the corner counties. Limestones low in magnesium and mostly of high purity outcrop near the Mississippi River north of Cape Girardeau and extend to the northern part of Jefferson County; they are exposed again near the Mississippi in Lincoln, Pike, Ralls, and Marion Counties. High-calcium limestone also covers extensive areas along the Mississippi and Missouri Rivers and in southwestern counties. Limestone also occurs in the northern and western parts of the State. Recent lime production has been confined to Greene, Lawrence, and Newton Counties in the southwestern corner of the State and to Marion, St. Francois, and Ste. Genevieve Counties in the east.

Commercial limestones occur in the eastern third of Kansas, but only those of Bourbon County have been used for lime. Rocks in the central area contain limestone, but little economic use has been found for them.

The principal limestone area of Arkansas lies in the Ozark Plateau region in the northern part of the State. High-calcium rocks suitable for manufacturing lime are found in several formations.

The commercial limestones of Louisiana are limited to two occurrences - one in Winn and the other in Evangeline Parish - and both have been used to produce lime. On the Gulf coast oystershells are used for making chemical lime.

The largest limestone area in Oklahoma is in the Arbuckle Mountain district; smaller areas occur in the foothills of the Wichita Mountains, in the northern and southeastern sections, and in the Ozark uplift. Lime has been produced in several locations, but recent output has been confined to Sequoyah County.

Limestones are distributed widely in Texas, particularly in the eastern half of the State. A belt runs from Red River in the northeastern part westward across the central part of the State and extends south and southwest, terminating a little southwest of San Antonio. Analysis of the stone show a content of 70 to over 90 percent calcium carbonate and very little magnesium. West and parallel to this formation is another group of limestones, and still larger areas are exposed in the Edwards Plateau west of San Antonio. Several lime plants are operated in the east-central district, chiefly in Comal, Travis, and Williamson Counties, and in western Texas near El Paso. A plant near Houston and one in Corpus Christi utilize oystershells for lime.

Montana limestone occurs chiefly in massive beds along the flanks of the mountain ranges in the western part of the State. Production has recently

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been centered at Anaconda and Elliston, Cochise County. Smaller deposits throughout the eastern two-thirds of the State have been used locally for lime burning.

Limestones are found in many parts of Wyoming but have not been developed extensively. The best-known deposits are in Albany, Laramie, and Platte Counties in the southeast and in Weston County in the northeast. Most of them are of the high-calcium type and supply stone for sugar factories.

The Colorado limestone deposits may be divided into two groups - an eastern division forming a belt immediately east of the Front Range and a second division lying west of the range. Limestone of the first division outcrops continuously from north of Fort Collins to the middle of Douglas County, passing a little west of Denver. The best rock contains over 90 percent total carbonates, but most of the formation is mixed with shale. Stone for lime manufacture is obtained chiefly in El Paso, Pueblo, and Chaffee Counties in central Colorado. Some of the limestones west of the range are pure enough for the highest-grade uses, but their location has discouraged commercial development. Other deposits outside these areas that have been exploited for the manufacture of lime are in Larimer County in the north-central part of the State and in La Plata County in the southwestern part of the State. Waste travertine from the building-stone quarries at Salida, Chaffee County, has been utilized for lime.

Very little is known of the chemical and physical properties of the limestone outcrops in New Mexico. Lime has been produced in San Juan and San Miguel Counties.

Western and Pacific Coast States

Limestone deposits are present in many parts of Idaho, the most valuable occurring in the southeastern and northwestern counties. Lime has been produced in both sections. Pure limestone from Butte and Teton Counties is shipped to sugar factories in Idaho and Utah. The most important limestones of Utah occur in many parts of the Wasatch Mountains in the northern and north-central counties. Many of them are pure enough for manufacturing lime, and there were a number of lime plants in this district in past years. Lime was produced also in the western and southwestern parts of the State.

Limestones of good quality are widely distributed in Arizona. There are lime plants at Paul Spur, Cochise County; Globe, Gila County; and Nelson, in the extreme northwestern corner of Yavapai County.

The principal lime plants of Washington are on Orcos and San Juan Islands, San Juan County, where the abundant crystalline limestone is used to manufacture a pure lime. Water transportation assists marketing. Lime is made from marble in Stevens County, and has been burned from suitable limestones in Chelan, Ferry, Okanogan, and Whatcom Counties. Limestone deposits occur also in the northeastern counties of Washington.

In Oregon, limestone pure enough for lime manufacture occurs principally in the southwestern and northeastern counties, and deposits in these sections

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have been used. Some of the stone in the southwestern area contains only 5 percent or less impurities. Limestones occur also in the northwestern corner of the State but generally are too impure for making lime.

High-calcium and magnesium limestones are available in various places in the eastern third of Nevada, and lime plants have operated in Clark and White Pine Counties.

Few extensive limestone deposits comparable with those in many of the Eastern States occur in California. Most of the deposits are irregular bodies of variable magnesium content. Lime is manufactured chiefly in the central part of the State. The extreme northern parts and the desert regions in the south have larger deposits of limestone than the more populous areas; but, because of the distance from markets and inadequate transportation facilities, they have little commercial value. However, lime has been produced in Siskiyou and Shasta Counties in the northern section and in San Bernardino County in the south. Oystershells are used as raw material in Alameda County. Present production is chiefly from Alameda, Eldorado, San Bernardino, Toulumne, Monterey, and Placer Counties.

USES

Lime is a raw material essential for numerous industries. It enters three large fields - the chemical and manufacturing industries, the building industries, and agriculture. For many years the building trades consumed the largest quantity, but the trend is toward wider use by the chemical and manufacturing industries. In 1906, the first year in which sales by uses were reported, 87 percent, by value, was consumed in building and only 8 percent in chemical and manufacturing processes; in 1940, 32 percent, by value, was used in building and 61 percent in chemical and manufacturing processes; and in 1950 only 27 percent was used in building and 67 percent in chemical and manufacturing processes. These figures are for lime exclusive of dead-burned dolomite. The percentage sold for agricultural purposes has shown only slight change - in 1906 about 6 percent, 1939 about 8 percent, and 1950 about 6 percent.

Of the total quantity of lime sold or used in 1950 (exclusive of dead-burned dolomite), 33 percent, by weight, was hydrated lime.

Much information on the chemical uses of lime is contained in a recent publication of the National Lime Association.8/

Industrial and Chemical Processes

Lime is one of the most widely used chemical reagents in the industrial world. It is utilized in many manufacturing processes and enters directly into the manufacture of hundreds of articles. The processes involved in the manufacture of products in which lime is used include neutralization, coagulation, distillation, precipitation, solution, hydrolysis, dehydration, high-temperature processes, high-pressure processes, gas absorption, saponification, and causticization.

8/ National Lime Association, Chemical Lime Facts: Bull. 214, 1951, 42 pp.

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Obviously, the kind of lime employed depends on the purpose for which it is to be used. Under some conditions, either high-calcium or magnesium lime can be used with equal success; under others, magnesium is objectionable. Quicklime is preferred for some processes and hydrated lime or ground limestone for others. Some of the industries and processes that consume large tonnages of lime are discussed in this paper, and general specifications of lime best-adapted for each are given. Lime, however, is used in so many processes that all of them cannot be included.

Metallurgy

Large quantities of lime are employed in the metallurgical industries. When pig iron is refined to make steel, the object is to eliminate certain materials that are undesirable or present in excessive quantities. Lime is used principally as a fluxing agent in the basic open-hearth process. It forms a basic slag for removing phosphorus and other impurities. The amount of lime used depends upon the quantity and nature of the impurities to be removed. In some localities limestone is used instead of lime. High-calcium lime low in alumina, silica, and sulfur is preferred. Magnesia is undesirable, as it does not eliminate phosphorus.

The requirements for lime (limestone) in the blast furnace are not nearly so exacting and are controlled chiefly by costs. As the stone used decreases in purity, the amount of stone and, consequently, the amount of fuel increases, but the lower cost of impure limestone may more than offset the added cost of fuel and larger quantities of stone required. In general, a stone carrying less than 1-1/2 or 2 percent impurity is preferred, but a stone having as high as 5 percent impurity may be used if it is easily obtained at low cost.

The relative advantage of using high-calcium or dolomitic lime in the blast furnace is an unsettled question. High-calcium lime or limestone is generally preferred, but there is a trend toward wider use of dolomitic limestone. Magnesia gives a more fluid slag, but it does not remove sulfur and phosphorus as efficiently.

Lime may serve several purposes in concentrating ore minerals in flotation. Material is now generally floated in slightly alkaline pulps where lime has advantages over soda ash or caustic soda under certain conditions. Lime is used rather extensively in the cyanide process.

Lime is employed also in a number of processes in manufacturing iron and steel products. The molds in which pig iron is cast are coated with lime to prevent the iron from sticking, either by spraying them with a wash or by passing the molds through milk-of-lime. Lime requirements for this are not very rigid, but the lime should form a slow-settling suspension and not contain too high a percentage of waste.

Lime is used to neutralize the "pickling" liquor that removes rust and scale from iron and steel before it can be discharged into streams. Milk-of-lime is used, and it should not settle rapidly and should not contain a high percentage of core or overburned material.

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Lime is used for several purposes in wire drawing. The rods of iron or coils of wire are dipped in milk-of-lime to neutralize the acid remaining after pickling. This lime coating serves as a lubricant in the drawing process and protects the finished wire from oxidation. Lime for this process must contain no grit or ash and must form a slow-settling suspension.

Lime is used in three processes for making metallic magnesium: The Dow method from natural brines; the Dow sea-water process; and the ferrosilicon (Pidgeon) process. Details of the reactions have been published.9/

Refractory Brick

Large tonnages of lime also are sold for the manufacture of silica brick, which is used chiefly for lining furnaces. Milk-of-lime is added to silica in quantities ranging from 1.5 to 4 percent CaO. The mixture is molded in forms, dried, and calcined under carefully controlled conditions. The lime serves as a bonding agent and also acts as an accelerator in the conversion reaction. Either quicklime or hydrated lime may be used for the milk-of-lime; however, it must be substantially free from ash, dirt, and core and must conform to the following requirements as to chemical composition, calculated on a nonvolatile basis.10/

		Percent
Calcium oxide (CaO)	minimum	92.0
Magnesium oxide (MgO)	maximum	3.0
Combined iron and aluminum oxides (Fe_2O_3) and (Al_2O_3)	do.	1.5
Silica (SiO_2) and insoluble matter	do.	3.0
Carbon dioxide (CO_2)	do.	
If sample is taken at place of manufacture		5.0
If sample is taken at any other place		10.0

Dead-burned dolomite, used extensively as furnace refractory, is not a true lime but sometimes is classed as refractory lime.

Paper

Paper manufacture is another large lime-consuming industry. Lime is used in several chemical processes to prepare the raw materials. In what is known as the sulfite process, it is combined with sulfur dioxide to form an acid liquor that at high temperature and pressure dissolves and removes all the constituents of the wood chips except the cellulose. Either quicklime or hydrated lime may be used; but, in either case, a dolomitic lime is preferred because magnesium bisulfite is more soluble than calcium bisulfite, its decomposition products are more soluble, and it produces a softer, whiter pulp. The ratio of magnesium oxide to calcium oxide should be reasonably constant, and the lime should be moderately free from impurities. The

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9/ Work cited in footnote 7, pp. 9-10.

10/ American Society for Testing Materials, Standard Specifications for Quicklime and Hydrated Lime for the Manufacture of Silica Prick (C49-24): 1924 Book of A.S.T.M. Standards, pt. 2, Philadelphia, 1939, p. 34.

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chemical composition of quicklime must conform to the following requirements, in percent, calculated on a nonvolatile basis.11/

	Calcium lime		Magnesium lime	
	Maximum	Minimum	Maximum	Minimum
Calcium oxide	-	94.3	-	56.5
Magnesium oxide	2.6	-	-	40.4
Oxides of silicon, iron and aluminum	3.1	-	3.1	-

In the soda process, wood and other fibers are digested with a caustic soda solution. Lime is used as a causticizing agent in recovering the caustic soda from the wash by liberating the sodium hydroxide. It serves the same purpose in recovering the sodium sulfate in the sulfate process. Either quicklime or hydrated lime can be used, but quicklime generally is preferred because the heat generated by its slaking hastens the reactions. It must be low in magnesia, highly reactive chemically, quick settling, and quick slaking and have an available lime content of 85 percent or more.12/

Rags for paper manufacture are cooked in a digester under steam pressure with lime or lime and soda ash. They are then washed to eliminate as much of the noncellulose material as possible. The standard quicklime used to cook rags must contain 90 percent available lime calculated upon the basis of the weight of the sample taken at point of manufacture. Hydrated lime must contain 64.3 percent available lime calculated upon the same basis.13/

Calcium carbonate or precipitated whiting is being used as a filler in magazine and book papers. A white product is obtained by precipitating or recarbonating milk-of-lime. The paper companies that use this material purchase quicklime and carbonate it in their own plants.

The Howard process, a development in utilization of waste sulfite liquor, involves treatment with a caustic lime reagent, which results in the production of calcium sulfite, an organic product (the lignin component) in solid form and a process effluent containing the carbohydrates, hemicelluloses, fats, etc. This treatment reduces stream pollution, in addition to yielding several valuable materials that can be processed further. Vanillin can be produced from the lignin material, and a substance with tanning properties usable in the leather industries is obtained also.14/

11/ American Society for Testing Materials, Standard Specifications for Quicklime for Sulfite Pulp Manufacture (C46-27): 1927 Book of A.S.T.M. Standards, pt. 2, Philadelphia, 1939, pp. 36-37.

12/ National Lime Association, Lime - Its Use and Value in the Industrial and Chemical Processes: 1930, p. 15.

13/ American Society for Testing Materials, Standard Specifications for Quicklime and Hydrated Lime for Use in Cooking of Rags for the Manufacture of Paper (C45-25): 1925 Book of A.S.T.M. Standards, pt. 2, Philadelphia, 1939, p. 35.

14/ Skinner, H. J., Waste Problems in the Pulp and Paper Industry: Ind. Eng. Chem., vol. 21, November 1939, pp. 1331-1335.

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Water Treatment

Lime, or a mixture of lime and soda ash, is used extensively for softening water. When water contains considerable quantities of the bicarbonates and sulfates of calcium and magnesium it is "hard." The carbonates of calcium and magnesium are very slightly soluble in pure water; but weak carbonic acid, formed when carbon dioxide comes in contact with the water, dissolves and holds calcium and magnesium in solution as bicarbonates, thus producing temporary hardness. When an excess of lime is added to hard water, it combines with the bicarbonates present and forms carbonates.

As calcium and magnesium carbonates are virtually insoluble, the reaction causes their precipitation, thus removing temporary hardness. Lime is used also as a coagulant for waters high in magnesium salts and for its bactericidal action.

The character of treatment depends on the nature of the raw water and the purpose for which it is to be used - whether for human consumption or for industry. The essential features of the process involve preliminary settling of the water in large reservoirs and the addition of lime and other materials, such as soda ash, iron salts, or alum, to coagulate the impurities and remove temporary or permanent hardness.

The only useful constituent of lime for treating water is the calcium oxide capable of reacting with the chemicals that are already in the water or that are added to it. Inert material makes more sludge to be disposed of and thus reduces the capacity of the equipment in which it is used, therefore, the lime must be substantially free of core, ash, and dirt and capable of disintegrating in water into a suspension of finely divided material. Standard quicklime for water treatment must contain 90 percent available lime, calculated upon the basis of the weight of the sample taken at the point of manufacture.15/ Hydrated lime for water treatment must contain at least 68.1 percent available lime.

Glass

There are many kinds of glass, and raw materials and processes used in their manufacture vary. Lime is employed as a raw material in plate, sheet, and bottle glass and a large proportion of the pressed or blown glass. The chemical requirements of the lime depend on the kind of glass to be produced. The National Lime Association gives the following requirements.16/

For optical glass, the iron oxide should be virtually zero, whereas in bottle glass 0.5 percent is permissible, with nearly the same limits for blown or sheet glass. The silica or alumina may run as high as 15 percent for bottle glass, but it should be very much less for the other grades of glass. The sulfuric and phosphoric anhydride should be low, not exceeding

15/ American Society for Testing Materials, Standard Specifications for Quicklime and Hydrated Lime for Water Treatment (C53-39): 1939 Book of A.S.T.M. Standards, pt. 2, Philadelphia, 1939, pp. 42-43.

16/ See work cited in footnote 11, p. 23.

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1 percent for bottle glass and diminishing through the other kinds to about 0.2 percent for optical glass. The combined CaO and MgO preferably should be at least 89 percent for bottle glass, 91 percent for sheet glass, 93 percent for blown glass, 96 percent for rolled glass, and 99 percent for optical glass.

Quicklime should not contain over 3 percent and hydrated lime not over 5 percent carbon dioxide. The requirements regarding the state of division of the quicklime are variable, depending upon the conditions under which it is to be used; but, unless otherwise specified, it should pass a 12-mesh sieve.

Hydrated lime in varying percentages is used in admixture with plaster of paris for bedding plate glass on grinding tables.

Leather

In the leather industry lime is used in depilation. The skins are soaked in vats containing lime water to which such "sharpening agents" as arsenic sulfide, sodium sulfide, and sodium hydroxide sometimes are added. The lime swells and softens the epidermal cells and dissolves the mucous layer, so loosening the hair from the hide that it may be removed mechanically.

Either quicklime or hydrated lime may be used. It should have an available lime or calcium hydroxide content of at least 85 percent and should settle very slowly in suspension. The presence of magnesia and clay is injurious, because they not only diminish the amount of lime present but make the lime much more difficult to slake; iron oxides, although quite soluble, may become fixed mechanically in the grain of the hide and cause stains.17/ Use of hydrated lime would remove the objections to magnesia but not to iron. In making morocco leather, however, high-magnesium lime is used.

Calcium Carbide and Cyanamide

Calcium carbide is made by heating a mixture of lime and carbon (in the form of coke, charcoal, or anthracite) to a very high temperature. Calcium cyanamide is made by treating this fused mass with nitrogen, lime facilitating the reaction of the nitrogen with the carbide.

High-calcium quicklime is required for this. Magnesia and alumina are undesirable, and the phosphorus and arsenic content especially should be low to avoid acetylene explosion.

Alkali Works

In manufacturing sodium hydroxide or caustic soda, lime is added to a solution of sodium carbonate (soda ash) as a causticizing agent. The caustic liquor formed is then filtered or settled to obtain a clear alkali liquor, which upon evaporation forms the sodium hydroxide.

17/ Proctor, H. R., Principles of Leather Manufacture: 2d ed., D. Van Nostrand Co., New York, 1922, p. 121.

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Since the function of lime in this process is to furnish soluble alkali, a high-calcium lime must be used. Quicklime with an available lime content of at least 85 percent is preferred. Magnesia is inactive as a causticizing agent, and its content preferably should not exceed 3 percent.

Lime is added to crude coal gas to concentrate crude ammonia liquors, and it is used also in distilling these liquors to produce aqua ammonia, anhydrous ammonia, or ammonium salts. The quicklime used in these processes should contain not less than 90 percent available calcium oxide; at least 95 percent of the lime after being slaked should pass a 50-mesh sieve, and not more than 10 percent should be retained on a 200-mesh sieve.18/

Sugar

Milk-of-lime is used to clarify and purify beet and cane juice used to manufacture sugar. When added to the juice and heated almost to boiling, it combines with the acids, breaks up and precipitates other organic compounds, and forms insoluble salts. When beets are used, the lime forms an insoluble compound with the sugar, and the juice is treated with carbon dioxide to disintegrate the lime and sugar and throw off the lime as calcium carbonate. This precipitate carries off all suspended matter, leaving a clear solution of sugar. In the Steffen process, ground quicklime is used to precipitate sugar from impure molasses. Because carbon dioxide is employed to clarify beet sugar, factories using beets produce their own lime, use the carbon dioxide obtained from the kilns for the carbonation process; manufacturers of cane sugar on the other hand buy their supplies of lime. Lime also is used in small amounts in refining sugar. The raw sugar is reduced to a syrup, which is treated with milk-of-lime and phosphoric acid to carry off impurities as a precipitate.

This industry requires the purest grade of high-calcium lime that can be obtained, except in the Steffen process, using quicklime or hydrated lime. According to specifications recommended by the National Bureau of Standards,19/ the hydrated lime should be of such size that 98 percent of it will pass a 200-mesh sieve; lime powder or ground quicklime should be of the same fineness but not so fine that it will ball when rotated in a 40-mesh bolter at 20° C. The lime must meet the following chemical requirements:

	Sugar soluble lime, minimum	Magnesium oxide, maximum	Loss on ignition, maximum
Quicklime for Steffen process..	90	3	2
Quicklime for other purposes ..	85	3	5
Lime powder	90	3	2
Hydrated lime	85	3	-

18/ National Bureau of Standards, Recommended Specifications for Quicklime for use in the Distillation of Ammonia from Ammonia Liquors Obtained in Coke and Gas Manufacture: Circ. 373, 1929, 6 pp.

19/ National Bureau of Standards, Recommended Specification for Limestone, Quicklime, Lime Powder, and Hydrated Lime for Use in the Manufacture of Sugar: Circ. 207, 1925.

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Paint

The simplest form of paint is whitewash prepared by mixing lime and water. Many whitewash formulas are used in preparing water paint for various applications, but the essentials are lime, pigment, and casein. Lime performs several functions in paint. As a protecting agent, soluble lime penetrates wood and then carbonates, protecting it against weathering and increasing its fire resistance. As an alkaline material, lime, or carbonate, prevents rusting of iron and corrosion of other materials. Because it is white and has good covering and working qualities, hydrated lime serves as an excellent, economical, and readily available pigment. Lime also functions as a cementing or bonding agent in paints, just as in plasters and mortars. Probably it also improves the disinfecting properties of paint and makes it more suitable as a sanitary coating.

In general, any hydrated lime that gives a smooth, fine-grained, slow-settling suspension may be used in paint. Selection of a particular lime for a given formula must be governed by the other components of the mixture and the use to which the paint is to be put.

Bleaching Powder and Bleach Liquor

Bleaching powder, chloride of lime, or chlorinated liquor is formed by the action of chlorine on moist, slaked lime. Liquid bleach is made by subjecting a milk-of-lime suspension to the action of chlorine. High-calcium quicklime or hydrated lime is used for these products. It should have no appreciable amounts of impurities, including magnesia, as they accelerate decomposition of the bleach.

Sand-Lime Brick

Sand-lime brick is made by mixing sand and lime (about 7-1/2 percent quicklime or 10 percent hydrated lime), pressing the admixture into brick form, and treating it with high steam pressure. The lime, reacting with a portion of the silica on the surface of the sand grains, forms calcium silicate, which binds the rest of the sand grains together. The lime must be completely hydrated before the mixture is pressed; otherwise, subsequent hydration will cause the brick to expand and rupture. For this reason, many manufacturers find it better to have their own hydrating plants. A high-calcium lime is required to insure proper hydration. The MgO content preferably should be less than 5 percent, and the lime must be highly reactive chemically.

Vienna Lime

Vienna lime is made from high-magnesium limestone or dolomite, with only traces of iron, silica, and alumina. The rock is grayish white and fine-grained and contains certain characteristic fossils (gastropods), which are said to affect its qualities materially. The stone is calcined carefully by a secret process, and the lime is cleaned, ground, packed in sealed containers, and sold to manufacturers of buffing compounds. Eardley-Wilmot states that the

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most important use of Vienna lime is for "coloring" nickel after it is plated to give it the deep, undersurface blue peculiar to the metal.20/

Synthetic Rubbers

Chloroprene polymers and butadiene polymers are two classes of synthetic rubbers in which lime is an essential raw material. The organic synthesis begins with acetylene, which is obtained through the reaction of water and calcium carbide, the calcium carbide having been produced from lime. The formation of acetylene from calcium carbide yields byproduct lime. Thus, the lime does not enter the rubber but initiates a series of organic reactions by forming a carbon compound (CaC_2) which reacts directly with the hydrogen of water to form acetylene.

Trade-Waste Treatment

A use of growing importance is that of applying lime to abate stream pollution at industrial plants. Its principal use is to neutralize sulfuric and other acids at steel, chemical, explosive, textile, and other factories. It also effects or aids precipitation of various waste products.

Building

For building lime, physical properties, such as plasticity, sand-carrying capacity, strength when mixed with sand, time of set, and color have primary importance. Either high-calcium or magnesium lime in the form of quicklime or hydrated lime is used in structural work, though for some uses one type may be preferred to another. If quicklime is used, it must be made into lime putty by proper slaking; it is also desirable to soak hydrated lime before use.

According to accepted specifications, quicklime for mortar, plaster, and masonry cement must have the following chemical requirements, in percent, calculated to the nonvolatile basis:21/

	Calcium lime	Magnesium lime
Calcium oxide ..... minimum	75	-
Magnesium oxide ..... do.	-	20
Calcium and magnesium oxides ..... do.	95	95
Silica, alumina, and oxide of iron .. maximum	5	5

If the sample is taken at the kiln, 3 percent is the maximum permissible CO_2 content; if taken at any other place, 10 percent is allowable.

The specifications for hydrated lime for structural purposes cover two kinds - masons' hydrated lime and finishing lime. Masons' hydrated lime may be used for scratch or brown coat of plaster, stucco, and mortar, and it may

20/ Eardley-Wilmot, V. L., Abrasives - Part I, Siliceous Abrasives: Canada Dept. Mines, Mines Branch Pub. 673, 1927, p. 97.
21/ American Society for Testing Materials, Standard Specifications for Quicklime for Structural Purposes (C5-26).

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be added to portland-cement concrete. According to the specifications for this type of lime, calcium and magnesium oxides should constitute not less than 95 percent of the nonvolatile portion, and carbon dioxide should not exceed 5 percent if the sample is taken at place of manufacture or 7 percent if it is taken at any other place. The percentages in both cases are based on the nonvolatile portion. The sample should leave a residue of not over 0.5 percent on a 30-mesh sieve and not over 15 percent on a 200-mesh sieve. Finishing hydrated lime is used, in addition to the uses of masons' lime, as an ingredient in the final or white coat of plaster, and it must have a plasticity figure of not less than 200 as tested with an Emley plasticimeter.22/

Mortar

Mortar is made by mixing lime putty with sand and water. For this lime putty is made by slaking quicklime properly or by soaking hydrated lime for an adequate time; the lime may be either high-calcium or dolomitic. The quality of a mortar depends on the preparation as well as on the characteristics of the lime used. The type of lime used ordinarily depends upon economic factors and local custom.

The quantity of mortar that a lime will produce varies widely with the properties of the lime. A properly burned, high-calcium lime will yield the greatest volume, provided the mortar is prepared properly. Magnesium or impurities will decrease the yield of paste. The mortar-making properties of various types of lime depend more on whether the lime putty was prepared from a properly slaked quicklime or from hydrated lime than on whether a high-calcium or a dolomitic lime was used.

As to the actual strength of lime mortars, tests conducted by the National Bureau of Standards indicate that mortar made of dolomitic lime is stronger than that made of high-calcium lime.23/ The strength of a mortar, however, may be controlled by the method of mixing and by the use of different kinds of sand. Properly made mortars are strong enough for ordinary building. Where factors of design or unusual conditions of service require high-strength mortar, portland cement may be added to lime mortar. The quantity of cement added is determined largely by the physical properties of the building units and the conditions of service. Depending upon use, the most common mortars employed are 1:1:6 and 1:2:9 cement, lime, and sand mixtures.

Masonry Cement

Lime has properties that make it eminently desirable in cement mortars for masonry. Hydrated lime mixed with cement increases the plasticity of a mortar and makes it denser, increasing its imperviousness to water. A cement mortar containing lime also adheres better to the brick. Cement can be replaced by hydrated lime without material diminution of strength if the ratio of hydrate to cement is less than 1:3, by weight.24/ Cement mortar, however,

22/ American Society for Testing Materials, Standard Specifications for Hydrated Lime for Structural Purposes (C6-31).

23/ Emley, W. E., and Young, S. E., Strength of Lime Mortar: Proc. Am. Soc. Test. Materials, vol. 14, pt. 2, 1914, pp. 339-358.

24/ Emley, W. E., The Use of Hydrated Lime in a Portland Cement Mortar: Proc. Nat. Lime Assoc., vol. 12, 1914, pp. 258-270.

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is much stronger than is necessary for ordinary buildings, and this feature ordinarily is not a factor to be considered. Either high-calcium or magnesium lime may be used in masonry cement.

Plaster

Lime plaster is made by mixing lime putty and sand, with or without hair. Coarse sand, often mixed with gravel, is used for exterior work, as for stucco, while fine sand is preferred for plaster for interior walls and ceiling. A highly plastic grade of lime is required for the finishing coat. It must be very nearly white, must work smoothly, and must not expand or shrink too much in setting. Many builders prefer hydrated lime for the finishing coat of plaster. If dolomitic lime is used, that which is prepared by pressure hydration is preferred.

Concrete

Hydrated lime increases the plasticity, smooth-working quality, and resistance to water absorption of concrete. It is added to the batch as it goes into the mixer.

Natural Cement

Lime added to natural cement increases the strength and plasticity of the mortar. A hydrated high-calcium lime is used; magnesia is objectionable because it is likely to hydrate after the cement has set, which weakens it. The lime may be added either as the cement is ground or when the mortar is mixed.

Artificial Stone

Lime is used as a binder in manufacturing artificial stone made of various sizes and types of aggregates. It produces a whiter and more pleasing product than ordinary portland cement. Color may be varied by adding appropriate quantities of mineral oxides.

Road Stabilization

An important use that began about 1945 is to apply lime to road bases and sub-bases for soil stabilization. This is particularly effective on certain clay or clay-gravel soils where the lime appears to react chemically with the silica and alumina in the soil, forming in effect a natural cement. It is regarded as a puzzolanic reaction. About 3 percent lime, by volume, ordinarily is added to the base-course materials.

Uses of Hydraulic Lime

Hydraulic lime is used principally to make masonry mortars or is blended with portland cement for concrete construction.

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Fertilizer

Lime is used primarily as a soil corrective and conditioner and secondarily to supply the plant-food elements calcium and magnesium. Soil is a complex material, having a number of chemical, biological, and physical properties, and lime may affect these properties by any or all of the following actions: (1) Neutralizing soil acidity; (2) replenishing the supply of calcium and magnesium; (3) promoting the activity of beneficial bacteria and depressing injurious soil organisms; (4) improving the texture and permeability of heavy soils by flocculating the colloids and clay particles; (5) hastening decay of organic matter and formation of nitrates; (6) rendering iron and aluminum insoluble, thereby preventing the phosphorus in the soil from combining with them in unavailable form, and preventing toxicity; (7) combining with nitrogen and phosphorus in easily available form; (8) acting as a germicide in certain soil-borne plant-disease organisms; and (9) leaving the soil in a well-balanced, productive condition.

Lime acts differently on various soils. The effects of the different types of limes on soils and plants and their use as quicklime, hydrated lime, or air-slaked lime, methods of application, and other factors for obtaining the best results have been subjects of careful investigation by agriculturists and chemists for many years. Their conclusions may be found in several publications listed in the bibliography.

Insecticides, Fungicides, and Disinfectants

Lime, dry or as whitewash, may be used as a mild disinfectant. It also is used in a number of insecticides, fungicides, and disinfectants sprayed on farm crops, gardens, orchards, and buildings.

Calcium arsenate, one of the more important insecticides, is used to control the cotton boll weevil, tobacco worm, potato beetle, and codling moth. A cold solution of arsenic acid is added to a diluted milk-of-lime, and calcium arsenate is formed as a white precipitate; this is filtered and dried, and the lumps are disintegrated to fine powder. In this process a slow-setting, free-slaking quicklime with an available lime content of at least 85 percent is used. Oxides of iron and alumina should be low, and the lime should be as free as possible from carbonates and other inert substances. Hydrated lime often is added to dry calcium arsenate as used, and this also should have a low magnesium content.

Commercial lead arsenate, containing small quantities of calcium arsenate and hydrated lime, is used for the same purposes as calcium arsenate. Lime sulfur, one of the best fungicides and insecticides for fruit trees, is prepared by heating sulfur with milk-of-lime. Bordeaux mixture is a basic sulfate of copper made by the reaction of copper sulfate with lime. Lime used in these mixtures is the high-calcium type with a low iron and alumina content.

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Recovery of Carbon Dioxide

During the past few years, interest in the recovery of CO_2 at lime plants has been stimulated by increasing use of carbon dioxide for refrigeration (dry ice), and several processes for its recovery have been developed. However, it is actually recovered at very few plants.

REUSE OF LIME

The recovery and reuse of scrap are important features of the metal industries, but the salvage and reuse of nonmetallic materials are usually quite unimportant. Ordinarily nonmetallic minerals cannot be recovered after having once been used. Lime, however, is reused to some extent.

In the paper-pulp industry, the hydrated lime employed to recover soda from the spent liquor used to digest wood chips, can be recarbonated for reuse by the following reaction: $Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3$. The calcium carbonate formed settles out as a sludge and may be recalcined after washing, filtering, and drying. Only small amounts of limestone are needed to supplement the lime recovered in this way.

A cyclic process also has been developed for using lime by the beet-sugar industry. The quicklime employed to precipitate sucrose from the aqueous solution of beet molasses is ultimately precipitated as calcium carbonate by adding carbon dioxide. The sludge is removed by filtering, the filter cake is calcined, and the CO_2 and quicklime are recovered for further use. The lime obtained by calcining the filter cake is said to be more active than that produced from freshly burned limestone.

Another instance of reuse has attained importance at municipal water-supply plants. When lime is added to water containing calcium bicarbonate in solution, it combines with the carbon dioxide to form calcium carbonate, which precipitates. When the carbon dioxide of the bicarbonate is thus removed, it also precipitates as calcium carbonate; consequently, large quantities of calcium carbonate sludge accumulate. Calcining this sludge to make lime, which is now being done at Miami, Fla., has the double advantage of utilizing a waste material profitably, and solving a serious waste-disposal problem.

In the paper-pulp and beet-sugar industries referred to earlier, the lime is gradually consumed as waste products are formed, and new lime from outside sources must be added continually. In the water-softening process, however, the quantity of recoverable lime constantly increases. The calcium carbonate that accumulates as sludge consists not only of the recarbonated product derived from the lime added to the water, but, in addition, the calcium carbonate that was originally present as bicarbonate in solution. Hence, more lime can be recovered from the sludge than was originally added to the water.

In manufacturing caustic soda and soda ash from common salt, the byproduct from the manufacture of soda ash is calcium chloride, but further processing of soda ash to produce caustic soda utilizes lime with the precipitation of calcium carbonate. The calcium carbonate could be reburned; but, at

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one plant using this process, the calcium carbonate is turned over to an adjoining portland-cement plant.

Other methods for reuse undoubtedly will arise as development of byproducts and studies on the elimination of wastes progress further.

TESTS AND STANDARDS

Standard methods of analyzing[25] limestone and lime have been devised, as have methods of sampling.[26] Methods for making physical tests also have been proposed.[27]

Certain standard specifications for lime for various uses have been published by the National Bureau of Standards[28] and by the American Society for Testing Materials in cooperation with the National Lime Association.[29]

The Federal Specifications Executive Committee has issued specifications for materials for purchase by Federal agencies;[30] Federal Specification SS-L-351 covers hydrated lime for structural purposes, SS-Q-351 covers quicklime for structural purposes, and SS-L-361 covers hydrated hydraulic lime.

The chemical analysis of a limestone is important in determining the properties of the lime it will yield, but physical properties are likewise quite important. The amount of crumbling or disintegration during calcination depends on the texture of the limestone, because the texture controls, to some extent at least, the moisture content and the thermal conductivity. However, slight textural differences may not be recognizable, even upon the basis of microscopic examination. Thus the calcining properties of a limestone are best determined by kiln tests.

Nevertheless, theoretical considerations are valuable in directing the trend of practical experimentation. One recent development has been the

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25/ American Society for Testing Materials, Standard Specifications for Chemical Analysis of Limestone, Quicklime and Hydrated Lime (C25-29): 1929 Book of A.S.T.M. Standards, pt. 2, Philadelphia, 1939, pp. 46-56.

26/ American Society for Testing Materials, Standard Specifications for Sampling, Inspection, Packing and Marketing of Quicklime and Lime Products (C50-27): 1927 Book of A.S.T.M. Standards, pt. 2, Philadelphia, 1939, pp. 58-61.

27/ American Society for Testing Materials, Tentative Methods of Physical Testing of Quicklime and Hydrated Lime (C110-38T): 1938 Book of A.S.T.M. Standards, pt. 2, Philadelphia, 1939, pp. 910-914.

28/ Copies of publications of the National Bureau of Standards and copies of Federal specifications can be obtained from the Superintendent of Documents, Washington, D. C.

29/ Copies of A.S.T.M. specifications may be obtained from the American Society for Testing Materials, 260 Broad Street, Philadelphia, Pa., or from the National Lime Association, 925 -15th Street, N. W., Washington, D. C.

30/ See footnote 28.

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laboratory study of lime and lime hydrate with x-ray crystallography.31/ These studies showed definite differences between the particle size (degree of crystallinity) of soft- and hard-burned limes. Likewise, the plasticity of lime hydrate depends on the size and shape of the crystal flakes, which in turn, seem to be controlled by the time of slaking.

PRODUCTION

Statistics

Lime statistics include refractory lime (dead-burned dolomite). Table 1 has been compiled to show the growth of the lime industry in the United States since 1925. The statistics included in this table are limited, with few exceptions, to open-market lime. Large quantities of lime are manufactured from stone either quarried by the producers or purchased and reported to the Bureau of Mines as limestone. Lime from these sources is not included in the table.

More-detailed statistics of lime by states and uses appear each year in the chapter on Lime of the Minerals Yearbook, published by the Bureau of Mines. The reader is referred to these chapters for current data on many phases of the lime industry.

Economics of Plant Location

The main factors to be considered in locating a lime plant are quality and extent of raw materials, conditions for quarrying, fuel supply, markets, and transportation facilities. The importance of considering carefully the character of raw materials available in relation to the type of lime in demand should be emphasized. The adaptability of limes for various products has been discussed on previous pages.

Size of Lime Plants

A statistical analysis32/ made in 1939 indicated that the number of lime plants had decreased greatly, but the capacity of individual plants had increased. According to the report, there were 1,073 lime plants in 1910, and their total production was about 3,500,000 short tons of lime. In 1938, the year preceding the date of that report, there were 284 plants, and production exceeded 4,100,000 tons. This trend has continued during subsequent years. In 1950 the number of plants had dropped to 168 while production had increased to nearly 7,500,000 tons.

31/ Clark, G. L., Bradley, W. F., and Azbe, V. J., Problems in Lime Burning. A New X-Ray Approach: Ind. Eng. Chem., vol. 32, July 1940, pp. 972-976.

32/ Bowles, Oliver, and Coons, A. T., Graphic Survey of the Lime Industry, 1910-38: Bureau of Mines Inf. Circ. 7088, 1939, 8 pp.

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TABLE 1. - Lime sold or used by producers in the United States 1925-50, by major uses, in short tons (includes quick and hydrated)

Year	Agricultural	Building	Chemical and industrial	Refractory[1/]	Total
1925	298,976	2,387,267	1,502,433	392,147	4,580,823
1926	297,010	2,320,323	1,556,350	386,715	4,560,398
1927	322,893	2,148,840	1,568,784	374,415	4,414,932
1928	333,910	1,986,465	1,689,276	448,761	4,458,412
1929	338,329	1,640,827	1,802,580	488,032	4,269,768
1930	343,111	1,204,614	1,488,415	351,740	3,387,880
1931	297,312	947,085	1,219,448	243,769	2,707,614
1932	244,574	596,825	982,858	135,733	1,959,990
1933	246,110	533,088	1,228,270	261,812	2,269,280
1934	222,077	511,419	1,338,723	324,868	2,397,087
1935	282,660	656,894	1,592,321	455,258	2,987,133
1936	336,905	891,267	1,924,460	596,751	3,749,383
1937	406,462	948,553	2,151,444	617,706	4,124,165
1938	364,312	854,461	1,761,555	366,626	3,346,954
1939	362,335	1,000,498	2,219,954	671,561	4,254,348
1940	364,823	1,010,435	2,643,762	867,909	4,886,929
1941	382,727	1,065,599	3,561,203	1,069,887	6,079,416
1942	400,631	697,677	3,776,126	1,229,357	6,103,791
1943	454,133	557,958	4,307,799	1,276,725	6,596,615
1944	466,390	520,000	4,196,383	1,290,790	6,473,563
1945	373,410	549,547	3,810,288	1,187,334	5,920,579
1946	384,658	845,604	3,684,455	1,077,983	5,992,700
1947	340,363	1,008,211	4,035,202	1,395,203	6,778,979
1948	323,300	1,140,518	4,255,403	1,544,755	7,263,976
1949	328,528	1,052,097	3,618,969	1,318,708	6,318,302
1950	332,687	1,248,989	4,137,297	1,759,443	7,478,416

1/ Dead-burned dolomite.

QUARRYING AND MINING LIMESTONE

Although limestones are widely distributed, only a relatively small number are suitable for manufacturing lime. The suitability depends on physical as well as chemical properties. Considerable variation among individual beds within the same deposit may occur, and this factor may determine the method of mining or quarrying employed or the suitability of the lime for various uses.

Methods of quarrying and mining limestone are discussed in two Bureau of Mines publications.33/ Both of these reports are now out of print but may be consulted at most large libraries. The methods will receive only brief mention in this report.

33/ Thoenen, J. R., Underground Limestone Mining: Bureau of Mines Bull. 262, 1927, 145 pp.
Bowles, Oliver, and Myers, W. M., Quarry Problems in the Lime Industry: 1927, 93 pp.

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Conditions Governing Open-Pit and Underground Work

Open-pit quarrying usually is to be preferred when the rock has little or no overburden, because blasting by modern methods in deep holes back of an open face is more economical than the more-confined drilling and blasting necessary in underground work. Where approximately horizontal beds are covered with a heavy overburden or where an opening in inclined beds must be carried beneath an ever-increasing burden of waste, underground methods are preferred. Underground methods are successful, however, only where the rock is strong enough to form a safe roof without timbering and with rock pillars spaced at moderate intervals.

Other important factors are the composition, structure, and physical properties of the various beds of a deposit. Certain beds may be unsuitable for manufacturing lime and should be discarded or diverted to other products. On the other hand, many deposits consist of a series of beds that, while varying somewhat in character, fall within the qualifications that permit utilization for lime. Selection of stone for a special kind of lime may necessitate a method of quarrying different from that followed when lime of another grade is to be produced.

Stripping

The stone must be stripped clean, for silica and alumina, the chief constituents of a sand and clay overburden, are harmful impurities in lime. Mechanical stripping is the most economical method if conditions are favorable, but it is sometimes necessary to strip irregular rock surfaces with large pockets of sand and clay by hand or to shoot overburden and rock down together and separate them later on the quarry floor. This process, however, is tedious and wasteful unless a washing plant is available. The difficulty of stripping rough surfaces may prompt operators to resort to underground mining.

Quarrying for a Uniform Grade of Lime

When the properties of stone at several levels or in several zones of a quarry face vary, rock of average quality with regular distribution of impurities that are not easily removable may be obtained only by mixing the stone from the various beds. In horizontal beds, uniform quality may be obtained by shooting down all the ledges together in a mixed mass, loading the rock by hand, and distributing successive cars from each loading point to different kilns. The finished lime also is mixed during loading. When conditions do not favor single-bench operation, a quarry may be worked in a succession of comparatively low benches, but work must be carried on simultaneously on all benches. Carloads of rock from the several levels then must be taken to the kilns in regular order. When beds are inclined, it is more difficult to maintain uniformity, and under some conditions underground methods offer advantages.

Quarrying for Special Kinds of Lime

Whereas efforts formerly were directed chiefly toward producing a single, uniform grade of lime, increasing markets for special kinds or grades have

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made it necessary for operators to select and quarry beds having the desired properties, as the quality of a lime depends principally on the quality of the parent limestone. Each kind of lime - high-calcium, dolomitic, plastic, or nonplastic - is used in different processes and products. The impurities and the percentage of each impurity in the lime also govern its use. As a rule, chemical uses demand greater purity than do agriculture or building; even small percentages of certain impurities may be decidedly harmful in some chemical processes.

The percentage of each impurity in a stone is virtually doubled in the lime. There is little or no loss of the main impurities during calcination, although the weight of the limestone is reduced almost half through loss of carbon dioxide. Approximately 56 pounds of lime is produced for each 100 pounds of limestone calcined. Therefore, if 4 percent is the maximum permissible percentage of an impurity in a finished lime, the proportion of this impurity in the limestone should not exceed 2 percent.

The physical as well as the chemical properties of a stone also influence the character of the lime produced. Limestones of identical chemical composition under the same burning conditions may give limes that differ in character. Some limestones crumble more readily than others during calcination. Certain beds chemically suitable may decrepitate or crumble so badly that it may be advisable to quarry and calcine them separately or, if lump lime is to be made, to reject them as raw material. Moreover, some beds are more refractory than others and require either a higher temperature or a longer time for calcination.

To obtain rock for special grades of lime, therefore, stone must be selected carefully in the quarry. Each bed may be worked as an independent unit, which may involve quarrying a succession of low benches and selecting and loading stone by hand. Underground mining sometimes is the better method. Rock from mines is not so liable to be mixed with impurities as that from open pits; this is particularly true of fines.

No general methods of quarrying can be given, for they must be varied to suit the peculiarities of the rock formation. Quarrying stone for specified types of lime usually costs more per ton than quarrying for a single uniform grade of lime, but the higher prices received for special grades may repay the increased cost of producing the raw material.

Transportation

Stone is removed from the quarry or mine, carried to the kiln or crusher, and elevated to the top of the kiln in a manner depending on the conditions in the quarry. Car and locomotive haulage has been replaced in many quarries by truck transportation. Cable cars are commonly used to convey rock up an incline to the top of the vertical kiln. Stone, 4 inches in diameter or larger, is preferred for shaft kilns because fines retard the draft.

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METHODS OF MANUFACTURE

Calcining Processes

Limestone is converted into lime by heat. The process brings the stone into contact with a sufficiently high temperature long enough to dissociate the carbon dioxide and drive it off as gas. The quantity of heat required varies with the chemical and physical properties of the stone; small pieces of stone calcine more quickly than large ones; fine-grained stone conducts heat more readily than that which is coarsely crystalline and porous. Experimental work[34] has shown that the temperature of dissociation of calcium carbonate is 898° C. (1,648° F.) at atmospheric pressure. The corresponding temperature for magnesium carbonate has not been determined as accurately, but 756° C. (1,393° F.), obtained by Mitchell, probably is correct. After the dissociation temperature has been reached, it must be maintained long enough to transfer the required amount of heat to the stone. A high temperature for a short time or a lower temperature for a longer time may be used, but the more nearly the heat approaches the minimum required the better the quality of the lime will be. To obtain a large output per kiln, however, 1,050° to more than 1,100° C. commonly is carried.

It is well-known that the chemical reaction involved in burning lime is reversible; that is, calcium carbonate may be decomposed into calcium oxide and carbon dioxide or these substances may recombine to form calcium carbonate. The factor that determines the way the reaction shall go is the pressure of the carbon dioxide. If the gas is allowed to accumulate, its pressure may reverse the reaction, and the lime will recarbonate. Therefore, prompt removal of the gas is essential to efficient calcination.

Calcination, commonly termed "burning," is done in some form of kiln. Shaft or vertical kilns are used most generally, although the use of rotary kilns is increasing, particularly when hydrated lime is to be produced from the quicklime. Pot kilns in which the stone and fuel are added in alternating layers were used some years ago, but very few are now operating.

Shaft Kilns

Shaft kilns are built in various designs; but, in general, this type of kiln is a short, wide stack lined with refractory material. Stone is dumped into the upper part, called the hopper, where it is preheated slowly by the hot, escaping kiln gases. It gradually slides down into the middle section of the kiln - the shaft - which is the burning or calcining zone. The lime manufactured in this hot zone sinks downward into the third section - the cooler - from which it is drawn at intervals. The size of a kiln usually is governed by the demand for the lime, because quicklime can be stored only a short time. Hydrated lime, however, may be stored for longer periods. If

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34/ Johnston, John, Thermal Dissociation of $CaCO_3$: Jour. Am. Chem. Soc., vol. 32, 1910, p. 938.
Mitchell, A. E., Studies on the Dolomite System, Part I - Nature of the Dolomite: Jour. Chem. Soc. (London), vol. 123, 1923, pp. 1055-1069.

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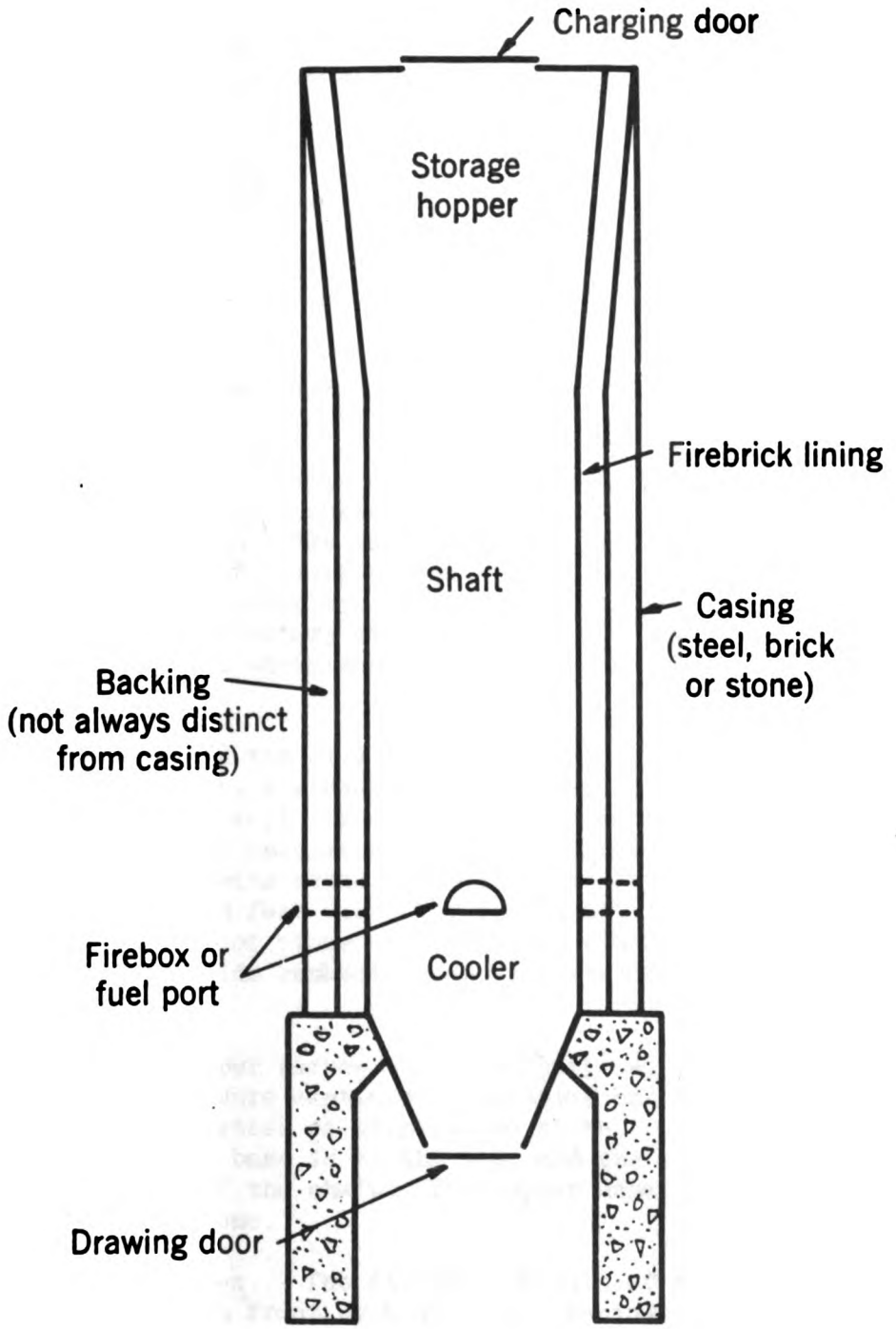

Figure 1. - Diagrammatic section of shaft kiln showing essential parts.

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there is a steady demand for a definite supply of lime, an operator may be justified in building a kiln large enough to furnish the desired quantity; otherwise it is better to build a number of small kilns so that production may be adjusted more easily. A generalized vertical section through a shaft kiln is given in figure 1.

Casing. - The casing or outside of a kiln may be of steel, stone (in older kilns), or a combination of steel with stone or some other material. It may be round, square, or elliptical. The casing performs three functions: It carries part of the weight of the kiln; protects the lining from changes in temperature; and minimizes the amount of heat lost by conduction and radiation.

Lining. - The lining usually is the same thickness throughout the kiln. If firebrick is employed, about 8 inches (two courses) generally are considered enough; other materials may range in thickness from 9 to 18 inches. The lining must be able to withstand the chemical action of the lime reasonably well, as well as the temperature required for burning and the abrasion to which it is subjected. The lining must be repaired or replaced at intervals. Various grades of firebrick generally are used; mica schist, sandstone, and granite sometimes are employed. Often two grades of firebrick are used; for brick refractory enough to give good results in the burning zone may be too soft to withstand the abrasion to which it is subjected in the upper kiln.

Top of Kiln. - The top of a kiln may be open, closed with flat steel plates, or surmounted by a stack. A closed top, used in some systems of induced draft, should be kept virtually airtight so that the fan that removes the gas need not handle unnecessary air. A closed top has two openings, one for charging the kiln with stone and one for removing the gas. The charging door usually is about 3 feet wide by 5 feet long, large enough to admit a carload of 2 or 3 tons of stone at once. The stack, which is the ordinary round-steel variety, aids combustion and assists in preventing recarbonation of the lime.

Hopper. - The hopper serves a twofold purpose, providing space for storing enough stone to insure continuous operation and conserving fuel by utilizing the heat of waste gases to preheat the stone. It is shaped like an inverted cone; the large base is at the top, and the sides slope until the cross section becomes that of the shaft. The hopper usually is large enough to hold a 48-hour supply of stone.

Shaft and Fireboxes. - The firebox consists of a grate spanned by an arch of firebrick, closed in front by a door and opening into the kiln in the rear. Two or more fireboxes are set into openings through the lining and casing in the lower part of the shaft, or, if gas or oil is used as fuel, ports through which it is led into the kiln are used in place of fireboxes. More and more kilns are now gas-fired. The proper grate area depends on the quantity and quality of coal burned; it is customary to allow 1 square foot of grate surface for 12 to 15 pounds of bituminous coal an hour.

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The draft caused by combustion of the fuel draws the flame up through the shaft in direct contact with the limestone, and the gases formed pass out the top of the hopper. The draft may be natural, forced by blowing air under the grates, or induced by a fan that draws the gas from the top of the kiln. By the Eldred process a fan takes the gas from the top of the kiln and forces it back under the grates. The carbon dioxide thus introduced is reduced to carbon monoxide (an endothermal reaction that tends to keep the grates cool); and as the carbon monoxide passes upward through the mass of stone it oxidizes (an exothermal reaction), thus extending the flame and promoting uniform calcination. Introduction of steam beneath the grates has the same effect.35/

The stone is heated gradually as it passes down through the shaft until the temperature of calcination is reached, which usually is about 8 feet above the grates. The cross section of the shaft may be rectangular, elliptical, or circular; its diameter is limited by the distance the heat can be made to penetrate toward the center. The size and shape of the shaft depend very largely on the method by which the kiln is to be operated.

Cooler. - The top of the third compartment or cooler has the same cross section as the shaft, but its sides recede to form a steep cone, which terminates at the drawing door built 3 or 4 feet above the floor. The lime falls through the door into large iron barrows or into dump cars on tracks beneath the kiln. When a lined cooler is used, the lime is removed hot and must be dumped to cool, which necessitates rehandling. When the lime is drawn cold, it may be dumped into a car for shipment. The most efficient coolers have ducts through which the air used in burning the fuel is drawn and thus preheated.

All unburned stone must be kept above the level of the grates, as heat from the fireboxes does not extend downward; enough lime, therefore, must be kept in the cooler to support the stone at the required height. Two methods of doing this are followed. When lime is drawn from the bottom of the kiln, the remaining lime and stone slide down and fill up the space. Because the flame and hot gases tend to pass up the sides of the shaft rather than through the center, unburned stone extends down farther in the center than at the sides. It is obvious, therefore, that, if the burned stone is allowed to fall to the burning level the unburned portion in the center falls below that level. By the "following" method enough lime is drawn so that the lowest part of the unburned material will reach to about grate level. The difficulty with this method is that the lime remaining above the grates may be overburned. By the "sticking" process the kiln is allowed to chill before drawing. The chilling causes the lining to contract and the fused compounds to solidify, owing to the action of lime on the lining. These two processes prevent the stone from following and cause it to "stick" or "hang." The lime is knocked down with bars, and an even layer of fresh stone falls to grate level. In general, stone will follow in a shaft with sides sloping outward and will stick if the sides are straight, but any type of kiln may be operated by either process.

35/ Berger, E. E , The Function of Steam in the Limekiln: Bureau of Mines Tech. Paper 415, 1927, 43 pp.

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After lime has been burned it should be kept moving through the kiln, as further heating impairs its quality. The frequency with which it should be drawn depends on many conditions and can be determined only through experience. Lime is sorted to remove underburned stone and overburned lime; this is done either while the lime is being drawn or when it is taken from the cooling floor.

Rotary Kilns

A rotary kiln is a steel cylinder resting on heavy steel rings or tires that encircle it and bear on steel rollers. It inclines about 1/2 inch to 1 foot and revolves slowly on its axis. The driving mechanism, consisting of a series of gears, is run by a variable-speed motor, whose speed is controlled automatically by the quantity of stone fed into the kiln.

Many years ago kilns ranged from 6 to 8 feet in diameter and 100 to 125 feet in length, but the more recent trend is toward larger and longer kilns. Firebrick are used for the lining in the calcining zone. The upper end of the kiln is a chamber, usually of brick, designed to collect and remove dust from the kiln. Beyond this chamber is the stack, which produces the necessary draft through the kiln and chamber. The cooler, similar in construction and operation to the kiln, though shorter and smaller, is placed beneath the kiln.

For rotary kilns stone must be uniform in size, generally 1/2 inch to 1-1/2 inches, which necessitates crushing and screening. For efficient operation the stone also should be clean and reasonably dry. It is charged constantly from a bin into the kiln by an adjustable feeder. To produce good-quality lime the heat of a rotary kiln must be uniform. Coal, oil, or natural or producer gas may be used as fuel. The burned lime is discharged from the lower end of the kiln through an opening in the lower part of the hood into a chute that directs it to the cooler. At the lower end of the cooler, it is discharged to a conveyor that takes it to a hydrate mill or to storage bins.

Sintering Machines

In 1925 and 1926, the Bureau of Mines, cooperating with a machinery company, conducted a series of tests to determine the feasibility of using sintering machines for calcining small stone. A sintering machine consists of traveling pallets with perforated floors. Limestone in small sizes is carried on the pallets and is calcined chiefly by hot gases from an external source; these are drawn through the layers of stone as the pallets pass over a suction box. Details of the operation have been described by Myers.36/ The equipment is employed by lime companies to a limited extent principally for making dead-burned dolomite.

36/ Myers, W. M., Manufacture of Lime from Small Stone with a Sintering Machine: Bureau of Mines Rept. of Investigations 2762, 1926, 15 pp.

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FluoSolids Process

One of the newer calcining methods is the FluoSolids process, which is used commercially by one company. The equipment consists of two units. The Fluodry unit is a steel cylinder 9 feet in diameter inside and 22 feet 6 inches high. Attached horizontally at the bottom is a combustion chamber 6 feet in diameter and 7 feet 6 inches long. The shaft is divided into two parts with a perforated firebrick dome. The lower section is the wind compartment and the upper the bed compartment. Both are lined with firebrick. Minus 6-mesh limestone enters through an 8-inch feed pipe at the top. In the bottom of the wind compartment is an oil burner and two air blowers, one to atomize the oil and the other to fluidize the stone. The exhaust gases and dust from the sizer are passed through cyclone collectors and scrubbers to the atmosphere. The sized and dried stone passes through a discharge valve.

Stone from this unit is then passed to the FluoSolids reactor - a vertical steel shell 13 feet 6 inches inside diameter and 45 feet high, closed at the bottom with a wind box having a perforated-steel constriction plate, and at the top with a steel cover provided with a take-off to the dust collector. It is lined with firebrick and divided with constriction domes into five chambers or stages: The top three chambers preheat the incoming stone, the fourth clacines it, and the fifth cools the lime. Oil burners heat the calcining compartment. When calcination is completed, the lime which fills the chamber to the overflow point, passes to the cooler, and additional stone descending through transfer pipes from the successive preheating chambers replaces it.

The major advantages of the process is fuel economy. Approximately 5,000,000 B.t.u. is required to calcine 1 ton of recoverable lime, whereas the rotary kiln requires 7,000,000 to 8,000,000. A disadvantage is the high dust loss; recovery of lime is only 78 percent of the total CaO in the stone. Means of obtaining a better recovery are being studied. The lime made is high quality.

The equipment has been described by White.37/ Further detail may be found by consulting published descriptions recorded by Bowles.38/

Other Developments in Technology

Much research and experimentation have been devoted to improving the efficiency of both rotary and vertical kilns. Methods and equipment used

37/ White, F. S., Operation of the Pilot-size FluoSolids Lime Reactor: Pit and Quarry, vol. 40, No. 7, January 1948, pp. 110-112.
38/ Bowles, Oliver, Cement Lime and Gypsum Papers Dominate A.I.M.E. Meeting: Rock Products, vol. 55, No. 4, April 1952, pp. 134-136.

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in calcination have been described in some detail by Azbe.[39] Other articles have appeared at time covering technologic advances in lime manufacture.[40]

A new type of calcining unit known as the Nelson that had been used in two lime plants in Mexico was introduced in a lime plant at Provo, Utah, in 1945. The unit is an inclined stationary furnace having a 35° slope. It is said to require little power or supervision and to be economical of fuel oil.

Another type of calciner known as the Ellernan is a vertical-type kiln in which the fuel is burned in a firebox at the side, and the hot gases are distributed throughout the stone by rows of tunnels at two levels. Cooling air is admitted through the lime discharge spouts and withdrawn through another set of tunnels. The kiln has continuous feed and discharge and uses stone of 1/2- to 1-1/2-inch sizes. Advantages claimed are uniformity of product and low labor costs. Several Ellernan calciners have been introduced in lime plants since World War II.

Fuel Efficiency

An investigation by the Bureau of Mines[41] indicates that greatest efficiency is obtained by using coke in shaft kilns. Average fuel ratios for bituminous coal are 3.58 pounds of lime per pound of coal for pot (mixed-feed) kilns, 3.37 for rotary kilns, 3.23 for shaft kilns (direct-fired), and 4.08 for shaft kilns employing producer gas. In general, pot kilns appeared more efficient than shaft kilns, and rotary kilns were least efficient.

Hydration Processes

Hydrated lime is prepared by crushing quicklime as it comes from the kiln, slaking it, and classifying the fine powder produced with screens or air separators to remove any core or overburned lime that would not slake. For hydrating, lime is crushed to about 1 inch or smaller, because, in these sizes, it may be slaked mechanically, its reaction with water is quicker, and it produces a better hydrate than does lump lime.

Lime and water are mixed for slaking in a mechanical device called a hydrator. There are various designs of hydrators, but they are of two general types. The intermittent type consists of a circular iron pan, which

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39/ Azbe, Victor J., Economical Manufacture of Quality Lime: Obtainable from the author, 8135 Forsythe Blvd., St. Louis 5, Mo.; see also articles by Victor J. Azbe in various issues of Rock Products.

40/ Avery, William M., Kelley Island Builds New Gas-Fired Shaft Kiln Plant at White Rock, Ohio: Pit and Quarry, vol. 41, No. 11, May 1949, pp. 94-96.
Searle, A. B., Verticle and Rotary Lime Kilns - Which Are Best: Cement, Lime and Gravel, vol. 21, No. 1, July 1946, pp. 6-15.
Anderson, A. H., The Travelling - Grate Coking Process as Applied to a Rotary Lime Kiln: Trans. Canadian Inst. Min. and Met. Eng., vol. 47, 1944, pp. 1-13.

41/ Moyer, Forrest T., Lime-Fuel Ratios of Commercial Lime Plants in 1939: Bureau of Mines Inf. Circ. 7174, 1941, 9 pp.

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revolves horizontally and is large enough to hold about 1-1/2 tons of hydrated lime, and a shaft with arms radiating from its lower end suspended in the center of the pan; the arms carry plows that scrape the bottom of the pan as it revolves, mixing the lime and water thoroughly. The pan is revolved until the evolution of steam ceases (indicating that hydration is complete) and the lime becomes light and dry. The machine is covered by a hood and stack. A continuous hydrator consists of long iron tubes, one above the other, in each of which is a screw conveyor. Lime is placed in the top tube, and water is added through a stack at one end of the tube. The lime and water are mixed by the screw conveyors as they are carried through the tubes. When the mixture reaches the end of the pipe, it is completely hydrated.

The hydrating process must be manipulated so that the lime may be slaked properly. It is important that enough water be added to hydrate the lime completely, but excess water makes the lime wet and sticky and must be avoided. About 18 pounds of water must be added to 56 pounds of pure, high-calcium lime to make 74 pounds of hydrate. It is necessary, also, that the water and lime be mixed thoroughly, otherwise the heat generated by slaking may be localized and become so intense that it will create undesirable working conditions. High-calcium limes slake much faster than those containing considerable quantities of magnesia and consequently in a short time liberate a great amount of heat, which must be dissipated. This may be accomplished by regulating the water in such a manner that the excess heat will be absorbed by evaporation. It is important also that the proper design of hydrator be used, for no one type is suitable for all kinds of lime.

Magnesium lime hydrates more slowly than high-calcium lime. Normal hydrated dolomitic lime consists of a mixture of calcium hydroxide and magnesium oxide with little magnesium hydroxide. However, by hydrating dolomitic quicklime in an autoclave under pressure, it is possible to produce a dolomitic lime that is almost completely hydrated. Pressure hydration is employed widely in dolomitic lime plants.

The chief advantages of hydrated lime to the consumer are that it is handled easily, keeps better than lump lime, does not require slaking, and generally has been freed from unburned or overburned lime by air separation. On the other hand, hydrated lime contains a considerable proportion of combined water, on which the consumer may pay freight.

Manufacture of Hydraulic Lime

Hydraulic limes are made by calcining siliceous or argillaceous limestones. The raw material may be calcined in a rotary or shaft kiln in the same way that ordinary limes are made, but the temperature required is somewhat higher. The resulting clinker contains enough lime silicates, aluminates, or ferrites to give hydraulic properties to the product, but it also contains so much free lime that the clinker will slake and disintegrate when water is added. Thus, the clinker requires no grinding. Slaking is the next step after calcining. If this operation is conducted carefully with just the proper amount of water, the resulting product will be a fine, dry, white powder - a mixture of lime silicate and hydrated lime.

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STORAGE AND SHIPMENT

Quicklime cannot be stored for a long time, as it air-slakes readily and eventually becomes useless for most purposes. It is marketed as lump lime, just as it comes from the vertical kiln, or as pebble lime from the rotary kiln. Also it may be ground or pulverized to any desired fineness. It may be shipped in bulk in airproof and moistureproof bags or in steel drums. It sometimes is shipped by truck rather than by rail; but, whatever the method of shipment, care must be taken that moisture does not reach the lime and slake it in transit.

Hydrated lime is taken from screens or air separators to dustproof storage bins. Here it may be aged if desired. Hydrated lime usually is shipped in 50-pound bags, which are packed by an automatic machine that receives the lime from the bins and delivers it to the bags.

MARKETS AND PRICES

The principal markets for lime have been indicated in the section of this report on Uses and by the tables of sales of lime, by uses, that appear annually in the Lime chapter in the Minerals Yearbook. Study of the statistics reveals that major sales have been to the building industries, for agriculture, to the steel and other metallurgical industries for refractory and fluxing material, to paper mills, and to glass, calcium carbide, and water-treatment plants. These industries normally consume 80 to 90 percent of domestic sales. The remaining 10 to 20 percent includes lime sold for use in manufacturing alcohol, alkalies, bleaches, calcium acetate, coke gas and byproducts, glue, insecticides, oils and fats, paints, rubber, and sand-lime, slag, and silica brick; in sewage and garbage disposal; in textile industries; and in wood-distillation and various other processes.

Cost of production is an influential factor in marketing. A plant that operates at low cost has a wider field than one that operates at high cost. The distance lime may be shipped depends also on the nature of the product. Lime peculiarly adapted for special uses may command a price that will justify shipment for long distances, and distant markets may be developed through an established reputation for reliability. Demands for lime conform in a general way to prevailing conditions within the more important consuming industries. For example, sales of building lime conform generally to the number of new residential units and sales of metallurgical and refractory lime to volume of steel-ingot production. Sales of lime are affected also by purely local conditions. Analyses of trends in sales, particularly of the causes for the fluctuations in quantities sold for the various uses, are valuable in forecasting future demands. Some of the findings of an analysis of market trends and prices of lime, compared with those of other materials, appear in a Bureau publication.[42/] Trends during succeeding years may be followed by consulting the Minerals Yearbook Lime chapters.

The average price of lime began to decline in 1924, more or less in conformity with prices of other commodities. This trend was arrested in 1934,

42/ Hatmaker, Paul, Trade Trends in the Lime Industry: Bureau of Mines Rept. of Investigations 3227, 1934, 18 pp.

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although the average was still considerably below values of predepression years. Prices have increased greatly since 1945.

Table 2 shows average values of lime sold for building, agricultural, and chemical purposes and the total average for a series of years. The figures in this table do not include the cost of containers.

TABLE 2. - Average value per ton of lime sold in the United States, 1914-50, by uses

Year	Agriculture	Building	Chemical	Total
1914	$3.13	$4.36	$3.68	$3.92
1915	3.21	4.26	4.03	3.98
1916	3.63	5.21	4.17	4.54
1917	5.07	6.63	6.35	6.29
1918	7.42	8.51	8.58	8.36
1919	7.63	9.64	8.49	8.84
1920	8.80	11.70	9.98	10.52
1921	7.86	10.70	9.19	9.83
1922	7.35	10.01	8.32	9.14
1923	7.59	10.57	9.18	9.81
1924	7.51	10.61	8.90	9.72
1925	7.12	10.10	8.64	9.30
1926	7.25	10.01	8.33	9.11
1927	6.93	9.76	7.94	8.75
1928	6.85	8.91	7.70	8.18
1929	7.06	8.72	7.33	7.84
1930	6.92	8.34	7.17	7.56
1931	6.47	7.33	6.70	6.90
1932	5.59	6.45	6.33	6.28
1933	5.36	7.18	6.11	6.28
1934	6.66	8.33	6.87	7.16
1935	6.73	8.70	6.50	7.28
1936	6.26	8.52	6.42	7.18
1937	6.74	8.66	6.47	7.30
1938	6.52	8.38	6.53	7.21
1939	6.11	8.56	6.23	7.06
1940	5.71	8.45	6.20	6.95
1941	6.24	8.69	6.23	7.06
1942	6.29	8.85	6.58	7.27
1943	6.90	8.70	6.93	7.44
1944	7.45	8.63	6.98	7.52
1945	7.78	8.93	7.21	7.76
1946	8.19	10.20	7.91	8.52
1947	9.28	11.46	8.63	9.42
1948	10.20	12.28	9.40	10.35
1949	10.79	12.97	10.00	10.97
1950	10.83	13.52	9.92	11.13

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FOREIGN TRADE

Imports of lime into the United States are relatively small, ranging during recent years from 20,000 to about 35,000 tons annually. Most of it enters from Canada to satisfy local needs in border States, particularly Washington.

Lime exports have increased considerably since 1945 but are still relatively unimportant. They range from 25,000 to over 60,000 tons a year. Canada and Latin American are the principal foreign markets. Figures for imports and exports appear annaully in the chapter on Lime in the Minerals Yearbook.

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